

A comparison between on-line and off-line tar analysis methods applied to common reed pyrolysis



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HIGHLIGHTS

- This study compares on-line and off-line analysis methods for tar characterization.
- On-line method is based on UV absorbance of tar in the gas phase using LEDs.
- Off-line method is based on CEN/TS15439, spectrophotometric and GC–MS techniques.
- Both methods show increasing absorbance at lower wavelengths and a peak at 600 °C.
- Both methods show a satisfying agreement between the estimated PAH concentrations.

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ABSTRACT

An innovative on-line tar measuring system has been tested using the reference standard for tar sampling (UNI CEN/TS 15439) and off-line analysis approach. Samples of common reed have been characterized by means of physical–chemical and thermal analysis. Several experimental tests have been performed with a bench scale pyrolysis apparatus setting different process temperatures (300–700 °C) and a heating rate of 50 °C min^{−1}. In each test the tar has been collected and analyzed. In addition, tars have been analyzed on-line by a lab scale fluidised bed gasifier – operated without the use of any gasifying agents – coupled with an optical measurement cell, equipped with Light-Emitting Diodes (LEDs) at different wavelengths (265 nm, 285 nm, 300 nm and 365 nm). The spectrum of absorbed light from the tar in the gaseous products has been detected through a photodiode. The total content of Polycyclic Aromatic Hydrocarbons (PAH) detected by the on-line method at 600 °C is 44 mg g^{−1} of initial feedstock, while the off-line method determined a total PAH content ranging from 2.75 mg to 74.41 mg at 300 °C and 700 °C, respectively. The integration between different analytical approaches on tar characterization has been useful to assess their capability and their potential application to predict tar composition.

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1. Introduction

In the last years, perennial grasses such as Switchgrass (*Panicum virgatum*), Miscanthus (*Miscanthus x giganteus*) and Reed canary-grass (*Phalaris arundinaceae*) have become of great interest as renewable energy sources, mainly because of their high productivity and low required energy input [1,2]. Therefore, together with traditional solid biomass (e.g., woodchips, wood and cordwood), which are products or by-products of forest management and timber industry they can be considered suitable fuels for heating purposes.

Similarly, emergent aquatic macrophytes can be regarded as local energy resources, mostly where they naturally grow in significant amounts. Wetland plants have a high macronutrient

accumulation capability because of their generally fast growth and high biomass production [3]. In particular, *Phragmites australis*, also known as common reed, is one of the most common plants living in wet ecosystems [4]. Even though this species has been extensively considered and studied for its phytodepuration potential, only few recent experiences concerning their energy utilization can be found in the literature [5–14]. The analysis of the product gas composition (e.g., its organic compounds content) obtained through pyrolysis or gasification is especially crucial to assess its suitability for further energetic applications. In this perspective, the optical analysis of the syngas has been widely investigated in the last years [15,16] and has led to encouraging results [17]. So far the most used technique has been the Infrared–Laser Induced Fluorescence (IR–LIF) which is a vibrational spectroscopy able to detect on-line the concentrations of the different gas components (CO₂, C₂H₄, O₂, CH₄, H₂O and H₂). LIF technique can be also applied to Polycyclic Aromatic Hydrocarbon (PAH) detection [18].

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In fact, it uses the spectral information from fluorescence spectra, that are characteristic for each tar species in the gas and the wavelength shift of the fluorescence signals even allows to separate fluorescence signals from the particles Mie scattering. Ultraviolet (UV) adsorption measurements do not offer these advantages but they reduce significantly the complexity of the measurement.

This work focuses on UV spectroscopy using lower energy light sources as Light-Emitting Diode (LED) [19]. This method is not focused on the permanent gas analysis but gives information on the tar content. The tar comprises a wide range of both low and high molecular weight organic compounds which condensate at ambient temperature and are responsible for the yield lowering of the syngas [20]. However, tar production might be lowered by controlling the operating conditions (e.g., temperature, heating rate). Furthermore, the characterization and quantification of tar produced during pyrolytic processes enables to assess the relative ease or difficulty of eliminating or processing it [21].

The aim of the present study is to compare conventional off-line with an innovative optical on-line method to characterize tars produced during pyrolysis of common reeds.

2. Materials and methods

2.1. Feedstock characterization

The biomass sampling activity has been carried out in China. Reed samples have been collected during a research expedition in Inner Mongolia province, in September/October 2011. In particular, the samples have been collected in the area of Wuliangshai Lake, located in the Bayannaoer Prefecture of Inner Mongolia Autonomous Region (China), at the Eastern end of the Hetao irrigation system.

The moisture content of the collected samples has been determined according to the UNI CEN/TS 14774-2. Subsamples were dried at 45 °C for 48 h until constant weight and ground with a Retsch Mill MM400. Ash content (UNI CEN/TS 14775), elemental composition (UNI CEN/TS 15104), sulfur and chlorine content (UNI CEN/TS 15289) and Lower Heating Value (UNI CEN/TS 14918) have been determined.

In addition, to fully characterize the thermal behavior of reed, thermal analysis has been performed using a Simultaneous Thermogravimetric Analyser (STA 449F3, Netzsch). This technique combines both the heat flux Differential Scanning Calorimetry (DSC) and Thermogravimetry (TG). STA analysis were performed at a constant heating rate of 20 °C min⁻¹ under inert nitrogen atmosphere from 30 to 1000 °C. The evolved gas was further characterized by a coupled Gas Chromatograph–Mass Spectrometer (GC–MS) and a Fourier Transform Infrared Spectrometer (FT-IR).

2.2. Pyrolysis tests and standard tar sampling

Several experimental tests have been performed in a bench scale pyrolysis apparatus setting different process temperatures (300 °C, 450 °C, 550 °C, 600 °C and 700 °C), setting the heating rate of the oven equal to 50 °C min⁻¹.

The bench scale pyrolysis apparatus – set up at the Free University of Bolzano and schematically presented in Fig. 1 – consists of a tubular electric furnace, a tubular reactor, a condenser, a series of impinger bottles for the collection of tars and a module for gas sampling and measurement. The furnace is able to reach the maximum temperature of 1050 °C. The reactor (20 mm diameter, 45 mm length) is placed inside the furnace; reactor and condenser are made out of quartz, which has a high resistance to temperature and chemicals, high purity and high stability.

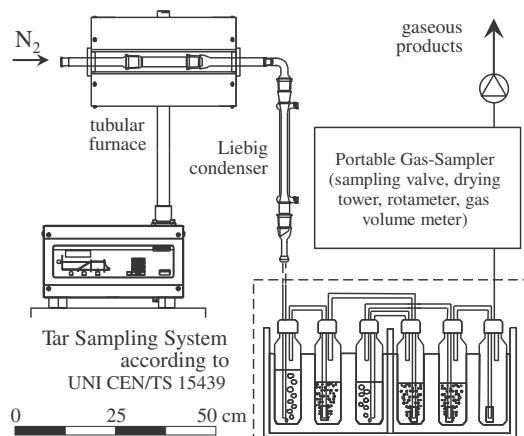


Fig. 1. Bench-scale batch pyrolysis system used for the off-line measurements.

The atmosphere inside the reactor is kept inert by nitrogen flow. The gas produced inside the reactor flows through the condenser, where it is cooled. The tar collection is then performed in a series of six impinger bottles, according to the technical specification UNI CEN/TS 15439; the first impinger bottle acts as a moisture collector; all the bottles except the last one are filled with isopropanol, an organic solvent suitable for tar capture. Except the first and the fourth, all the bottles are equipped with G0 frits (i.e., sintered glass filters with a nominal pore size in the range 160–250 µm); the first, the second and the fourth bottle are kept at 35/40 °C with water as cooling liquid, while the others are cooled at –15/–20 °C with a mixture of salt/ice/water. The gas suction device consists of a drying tower, a rotameter, a dry running rotary vane vacuum pump and a dry gas volume meter (measurement range: 0.4–6.0 m³ h⁻¹; accuracy: 0.09% at 1.2 m³ h⁻¹, –0.2% at 0.4 and 6.0 m³).

2.3. Off-line tar characterization

For each test, the tar–isopropanol solution has been collected and concentrated (total volume of 50 mL) using a rotary evaporator. The absorbance has been measured by means of an Hitachi U-2001 UV/visible spectro-photometer at 265 nm, 285 nm, 300 nm and 365 nm in agreement with the wavelengths of the light sources used in the on-line tests.

In addition, the tar solutions have been analyzed by GC–MS technique. PAH have been separated on a DB5 MS column (J&W Scientific) and detected by a high resolution ($R > 10,000$) mass spectrometer (GC–HRMS, MAT95XL, Thermo Scientific). PAH have been identified by the addition of deuterated internal standards. The detected PAH concentrations have been reported to the initial reed biomass sample (dry weight).

2.4. On-line tar measurement

Several experimental tests have been performed in an allothermal bench scale fluidized bed gasifier – operated in inert atmosphere without the use of any gasifying agents – coupled with an optical measurement cell, developed at the Institute of Thermal Engineering of the Graz University of Technology.

Reed samples (100 mg, approx. 2 cm large) have been introduced one-by-one in the reactor, which dimensions are 50 mm in diameter and 120 mm in height; this cylinder is then filled with 200 g of olivine sand. The fluidization agent (nitrogen) is preheated and injected into the sand bed from the bottom of the reactor, through a nozzle with six holes of 1 mm diameter.

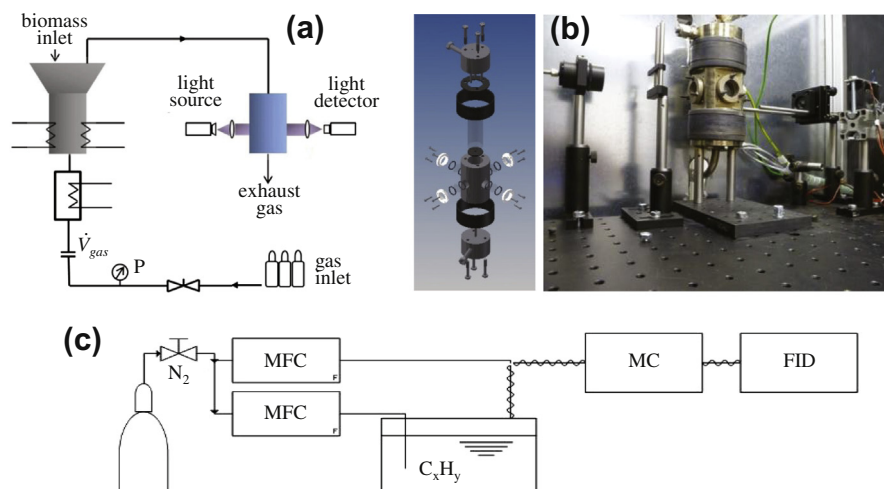


Fig. 2. On-line system devices: (a) fluidized bed batch reactor and measurement cell scheme; (b) optical measurement cell used for the on-line measurements and (c) synthetic gas mixing station with tar bubblers.

Table 1
Extinction coefficient ϵ , for different tar species.

Component	Structure	λ (nm)	$\ln \epsilon$
Phenol [24]		265	3.17
		285	2.64
		365	–
Indane [25]		265	3.03
		285	1.90
		365	–
Naphthalene [26]		265	3.49
		285	2.38
		365	–
Acenaphthene [27]		265	3.17
		285	2.64
		365	>0
Biphenyl [28]		265	4.00
		285	3.08
		365	>0
Acenaphthylene [29]		265	3.40
		285	3.30
		365	2.52
Anthracene [26]		265	>0
		285	>0
		365	2.81
Pyrene [30]		265	2.71
		285	3.22
		365	4.09

The whole system (gas preheater and reactor) is heated up thanks to 3 kW heating ropes equipped with thermocouples. The temperatures are monitored by means of a self-produced LabVIEW

software (Fig. 2a). The measurement cell (Fig. 2b) is composed of a heated pipe with four quartz windows placed at 90° between each other. During the operations the cell is constantly kept at 350 °C, in

Table 2
Chemical and physical characterization of reed tissues.

Moisture (%wt _{ar})	Ash (%wt _{dry})	C (%wt _{daf})	H (%wt _{daf})	O (%wt _{daf})	N (%wt _{daf})	S (%wt _{daf})	Cl (%wt _{daf})	LHV (MJ kg _{dry} ⁻¹)
5.4	4.4	47.8	6.4	44.6	0.3	0.3	0.7	16.85

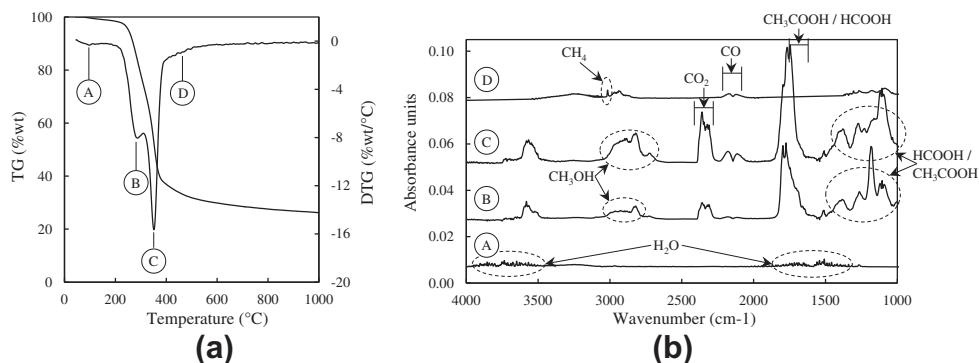


Fig. 3. Thermal analysis of reed: (a) TG and DTG curves and (b) FT IR spectra (A $\approx$ 97 °C, B $\approx$ 288 °C, C $\approx$ 351 °C, D $\approx$ 450 °C).

order to prevent any condensation and any influence of temperature variations on the optical measurements.

The outgoing gas from the reactor is driven into the cell through a 25 cm length of a 6 mm diameter stainless steel tube. In this way, the gas enters the measurement cell in less than half second preventing any side reactions (e.g. tar cracking). Moreover, thanks to the low Reynolds number (Re) inside the measurement cell (Re = 340, calculated for nitrogen at 300 °C) and to the small tube size, the flow can be considered laminar and the entrance region flow length is calculated of about 12 cm. The flow is consequently fully developed before entering the measurement cell.

The outgoing gas from the batch reactor enters the measurement cell from the top, flows on the central quartz tube and goes out from the bottom of the cell where it is condensed in cold isopropanol before entering the exhaust gas suction system.

During its passage through the measurement cell, the gas flow is crossed by a UV-light beam. The LED light source is placed on one side of the measurement cell, while, on the opposite side, a photodiode detector equipped with electronic amplifiers and focus lenses collects the light beam after the passage into the measurement cell. The UV-light radiation is produced using different LEDs. The light sources used in this work emit the following wavelengths: 265 nm, 285 nm, 300 nm and 365 nm. The first three are deep-UV LEDs with hemispherical lenses having a power range lower than 1 mW, while the near-UV LED (365 nm) reaches 25 mW. The UV-light absorption is caused by the presence of an instable double covalent bond and consequently all organic unsaturated components are visible, while permanent gas components are transparent [22].

During the reed samples pyrolysis process, the photodiode receives the light from the LED light source and it produces a voltage signal that is proportional to the light intensity that reach its surface. The voltage signal over the time has been recorded from a computer connected with the photodiode. In this way, the absorbance can be calculated as logarithmic ratio between the voltage values:

$$A_t = \log \left(\frac{V_0}{V_t} \right) \quad (1)$$

The absorbance value A at a certain time t , it is calculated as the logarithmic ratio between the initial voltage value V_0 and the voltage value at the time t , V_t .

The time needed to complete the process is slightly depending on the temperature but, in general, the pyrolysis of the small reed samples in a fluidized bed reactor can be considered completed in about 12 s. If the tar composition is not known it is difficult to translate this absorbance diagram in terms of tar concentration [23]. The reason is that more than one tar specie causes absorption at the same wavelength (e.g. 265 nm, Table 1).

However it is possible to normalize the composition on one tar component. For this purpose, the measurement cell has been previously calibrated employing a synthetic gas mixing station, equipped with tar bubblers. For this purpose the measurement cell has been connected with the synthetic gas mixing station and with a Flame Ionization Detector (FID) in series. Aim of the FID is to measure the real tar concentration of the obtained gas: this is possible because the gas contains just one hydrocarbon at a time.

Fig. 2c shows the scheme of the synthetic gas mixing station. One mass flow controller injects the nitrogen into the hot tar tank, while a second one is used as a dilution line. The slope of the calibration curve represents the extinction coefficient multiplied by the optical length, as described from the Lambert–Beer law:

$$A = \varepsilon l C \quad (2)$$

where A is the absorbance, C is the concentration (mol L⁻¹), ε is the extinction coefficient (L mol⁻¹ cm⁻¹) and l the optical length (cm).

The calibration lines [23] of the different tar components show also a good reproducibility and a low standard deviation (1.5% for naphthalene at 265 nm).

The total yield of organics products has been estimated in this way and compared with the standard sampling and off-line analysis methods.

3. Results and discussion

3.1. Reed characterization

The moisture and ash content, the lower heating value and the elemental composition of the tested reed samples are reported in Table 2.

Thermogravimetric (TG) and Differential (DTG) curves (Fig. 3a) show three main reactions. The first peak around 100 °C is due to water loss and can thus be attributed to the residual water content of the biomass. Water loss is followed by two reactions (B at

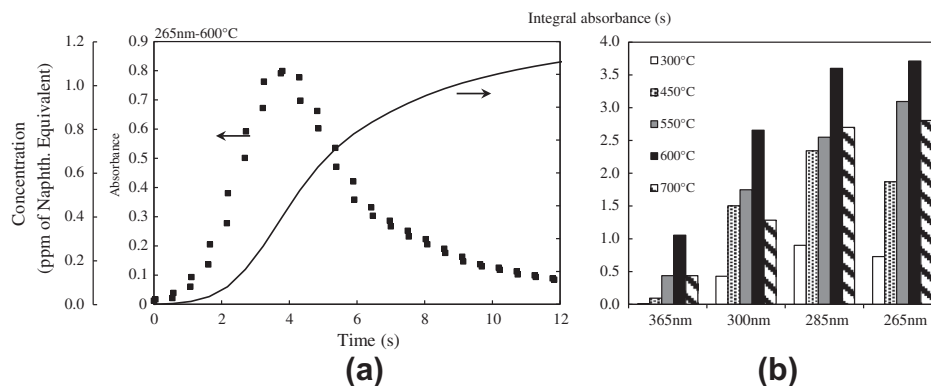


Fig. 4. On-line method: (a) absorbance at 265 nm and 600 °C and corresponding absorbance integral curve and (b) integral absorbance at different temperatures and wavelengths.

around 290 °C and C at around 350 °C) which are also due to the main weight loss during thermal degradation. The residual mass at 700 °C is about 29%.

In addition, for each sample, FTIR spectra have been recorded to define qualitatively the evolved gases during thermal conversion. Spectra were recorded at four selected temperatures, corresponding to the three main reactions during thermal degradation. Results are reported in Fig. 3b. The moisture loss of biomass sample attributed to the first peak (A) was confirmed by the FTIR spectra recorded at 100 °C. At higher temperatures, i.e. around 300 °C methanol (CH_3OH), acetic acid (CH_3COOH) and formic acid (HCOOH) could be detected. These three compounds are still present up to 350 °C but not at temperatures higher than 450–500 °C. In addition, carbon dioxide (CO_2) release increased from temperatures around 300 °C to temperatures around 350 °C and then decreased at around 450–500 °C. At this latter temperature methane (CH_4) could also be detected in the evolved gases. This is in accordance to thermodynamic equilibrium calculation, as well as the increasing trend of carbon monoxide (CO). In fact organic acids as acetic and formic acids together with non-condensable gases as CO , CO_2 and CH_4 are degradation products usually found during pyrolysis of lignocellulosic biomasses [31].

3.2. On-line and off-line absorption tests

UV Adsorption technique refers to a tar definition which includes all organic compounds from benzene (of molecular mass 78 g mol^{-1}) up to bigger molecules (with molecular mass of 300 g mol^{-1}). The preliminary tests for the calibration of the measurement cell (data not shown) prove that monoaromatic hydrocarbons (e.g. phenolic components) present higher response factors in the deep-UV range and that PAH (e.g. pyrene) have shown higher extinction coefficients in the near-UV, according to different literature data (Table 1).

Starting from the absorbance value (an example of absorbance diagram recorder at 600 °C and using the 265 nm LED is reported in Fig. 4a) and considering that the tar mixture has the same extinction coefficient of naphthalene, it is possible to calculate the tar concentration, as highlighted in the secondary vertical axes on the left in Fig. 4a.

The area under the absorbance curve is consequently proportional to the total amount of tar, released during the process. The integral value of absorbance (I_A) at a certain time t can be calculated as:

$$I_{A,t} = \int_0^t A dt \quad (3)$$

where

$$\int_{t_1}^{t_2} A dt \approx \frac{(t_2 - t_1)(A_{t1} + A_{t2})}{2} \quad (4)$$

The integral absorbance value is consequently not representing an absolute value of absorbance but the absorbance multiplied for the time in seconds, as shown in the secondary vertical axes on the right in Fig. 4a. The value remains however proportional to the total tar released and can be compared with the absorbance values measured spectrophotometrically on the liquid condensed tar samples.

For example, if the total area under the absorbance curve at 600 °C and 265 nm is normalized on naphthalene equivalent, the total tar released is 28 mg. This value is acceptable, considering that the initial sample is 100 mg. The total tar production, considering this case study and this normalization hypothesis, is therefore about 28% of the sample, while syngas and water represent the remaining 72% of the product, being the small char mass negligible. Finally, considering the big dilution, necessary for the fluidization of the sand bed (about 12 L min^{-1} for a theoretical calculated fluidization number ranging between 3 and 4), the average concentration of naphthalene equivalent is about 10 mg N m^{-3} .

Pyrolysis tests have been conducted at different temperatures (300 °C, 450 °C, 550 °C, 600 °C and 700 °C) and the final value of integral absorbance, measured at different wavelengths, is reported in Fig. 4b, showing how the total amount of tar produced is influenced by the temperature. In particular, at low temperature

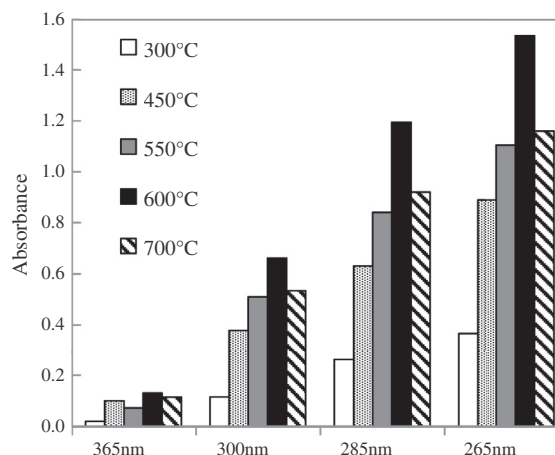


Fig. 5. Off-line method: absorbance of the condensed tar samples.

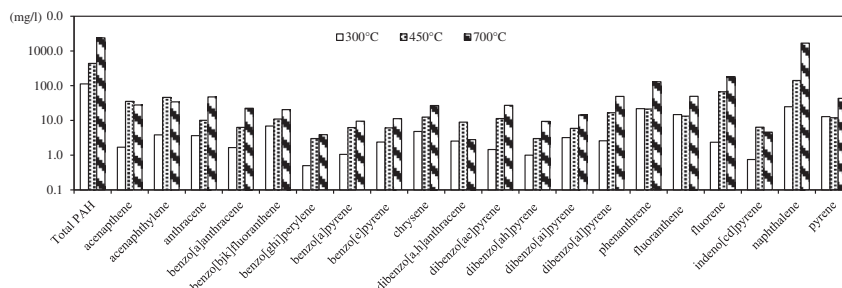


Fig. 6. Off-line method: PAH concentration in the condensed tar samples.

the production increases significantly (e.g. between 300 °C and 450 °C). Subsequently, there is a maximum of the tar release (600 °C) after which the concentration of tar decrease with the temperature. A similar behavior has been observed on a lab-scale fluidized bed gasifier, operating at the TU Graz with wood pellets [32].

Moreover, the 365 nm LED which is more sensitive to the PAH does not show any absorption for low temperatures but rather after 500 °C. This behavior can be easily explained with the tar maturation as reported by several authors [33,34]. At about 500 °C it is possible to observe a variation in the tar composition from 1st class oxygenated compounds to 2nd class hydrocarbons that are more visible at this wavelength.

The comparison between the results of absorbance on the condensates samples (Fig. 5) and the cumulative absorbance of the gas phase shows some clear analogies:

- in both cases there is a peak of tar production at 600 °C;
- lower wavelengths (deepest-UV) shows higher absorbance for each temperature;
- the smaller is the temperature the higher is the increasing of tar production for small temperature growths (e.g. between 300 °C and 450 °C respect to 450 °C and 550 °C);
- the ratio between the peaks are similar especially between the peaks at low temperature (e.g. 300 °C and 450 °C);
- the 365 nm led shows a clear response just above 500 °C, because at this temperature the production of PAH increase a lot, as shown from the GC analysis as well (Fig. 6).

3.3. PAH detection through GC–MS

The detected PAH concentrations are reported in Fig. 6. The main detected compounds are: naphthalene, phenanthrene, fluoranthene, acenaphthene, acenaphthylene, dibenzo[a]pyrene, indeno[1,2,3-cd]pyrene and pyrene. The total PAH concentration, as well as the concentration of most of the main compounds, shows a clear increasing trend with the temperature. This behavior is in good agreement with the literature [35].

The total PAH content has been normalized respect to the initial biomass sample, obtaining an increasing PAH yield with the temperature (2.75 mg g⁻¹, 15.84 mg g⁻¹ and 74.41 mg g⁻¹ at 300 °C, 450 °C and 700 °C, respectively). In pyrolysis tar, a PAH content ranging from 7.0% to 12.6% at 400 °C to 21.4% at 800 °C have been reported for lignocellulosics [36]. Referring to a value of 15.6% at 600 °C, a yield of 44 mg g⁻¹ has been estimated from the on-line measurement. This is in good agreement with the increasing off-line measured yield.

4. Conclusions

The comparison between on-line (UV LED absorbance) and off-line (CEN/TS 15439, spectrophotometry, GC–MS) methods for tar

characterization shows a good agreement between the detected absorbance values.

Both the approaches highlighted a peak at 600 °C and an increasing absorbance at lower wavelengths. A total tar yield of 280 mg, per gram of initial feedstock, for pyrolysis temperature of 600 °C has been assessed by the on-line method.

The performed analysis show also a satisfying agreement between the estimated PAH concentrations in terms of total production with respect to the initial feedstock mass, confirming an increasing trend respect to the pyrolysis temperature. PAH yields of 2.75 mg, 15.84 mg and 74.41 mg per gram of initial feedstock – at 300 °C, 450 °C and 700 °C, respectively – have been assessed by means of the off-line method, while a yield of 44 mg has been estimated by means of the on-line measurement at 600 °C.

The proposed on-line method seems particularly promising as it is based on a simple technology and can be applied onsite to real plants, in order to obtain quantitative tar measurements.

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